RED CERAMIC WITH ADDITION OF PETROLEUM COKE

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Abstract. The aim of this work was of evaluate the introduction of petroleum coke in a red ceramic. Petroleum coke is a solid fossil fuel, petroleum derivative, of black color and granular form approximately, obtaining as a byproduct from distillation of petroleum, by the process called "cracking" heat. This product represents from 5% to 10% of the total oil in the refinery. With percentage of 0%, 0.5%, 1% and 1.5% coke added into clay were obtained ceramic pieces. After drying at 110°C and firing at 750°C, 800°C and 850°C, were obtained the mechanical and physical properties and the Weibull distribution, used to evaluate the failure probability of the material. The results show the influence of petroleum coke in ceramics, suggesting introduce 1% of coke at 800ºC, when the Weibull modulus reaches value 9 (m=9).

Introduction

The issues of quality, energy and environment are assumed now as foundations of sustainability and consequent industrial competitiveness, in which the ceramic industry fits in this context [1]. Considering a better performance of its products and a reduction in costs, some ceramic industries have been using the petroleum coke as fuel and/or mixed the clay material.

The coke, trade name, is a solid fossil fuel, petroleum derivative, a black and approximately granular form or type "needle", which is obtained as a byproduct of petroleum distillation (at the bottom of the distillation column), in a process called "cracking" heat. The incorporation of waste in red ceramics currently presents as one of the main technology solutions for the disposal of industrial and municipal solid waste [2].

When manufacturing a certain component civil construction one has to evaluate what maximum stresses it should support component. With this information it is possible to choose the material to be used in the component. Red ceramic materials, the dispersion of the test results for resistance to rupture is evident, therefore, should be taken into consideration to evaluate which materials to be used according to firing temperature.

Was used Weibull distribution [3, 4] to evaluate the results. The Weibull distribution depicts the probability of the material fails when subjected to a given load level. This probability of failure of the material is subjected to tension σ is provided by Weibull probability function. The equation depicts the Weibull distribution [Eq.1]:

$$f(\sigma)=\frac{m}{\sigma_R}\left(\frac{\sigma-\sigma_0}{\sigma_R}\right)^{m-1}\exp\left\{-\left(\frac{\sigma-\sigma_0}{\sigma_R}\right)^{m}\right\} \quad (1)$$

Where σ_0 is the strain before which the material will not fail, σ_R is a referential tension value, corresponding to 0.632 probability of failure of the material is the Weibull modulus, related to the dispersion of the measurements.

In the Weibull distribution can be observed the behavior of fractures of ceramic red. This distribution connects the material failure and presence of defects which weaken. In direction, this work aims to characterize and observe the influence of incorporation of petroleum coke in the technological properties of red ceramic.

Materials and Methods

Materials

For this study, we used the following materials: clay used to produce red ceramics from the municipal district of Campos-RJ and Coke, of the distillation of Petroleum.

Methods

Characterization tests

Particle Size Analysis of the Coke and Clay

The tests performed showed the particle size distributions of clay and of the Coke also used by wet sieving and sedimentation for at LECIV/CCT/UENF, according to [5].

Quantitative Chemical Analysis

These tests were carried out in the laboratory characterization LECIV/CCT/UENF. The samples were sieved on #200 mesh (0.075mm). The equipment used was the florescence spectrometry Philips model PW 2400, on 10g of pressed powder pallets. The loss of ignition was obtained by determining the weight difference between samples fired at 950ºC and dried at 110ºC.

X-Ray diffraction

The qualitative mineralogical composition was obtained by X-Ray diffraction, Shimadzu equipment model DXR 7000, operating with Cu-Kα radiation and 2θ ranging from 5º up to 80º, for clay, and 5º up to 40º for coke.

Technological Tests

Sample Preparation

Samples for technological tests were prepared with clay and four different waste contents (i.e. 0, 0.5, 1.0 and 1.5%). The coke powder was sieved through #20 mesh (0.85mm). The batch mixture was performed on dried material and the extrusion moisture was calculated by Eq.2 [6]:

$$Wext. = \frac{LL}{2} + 2\% \qquad (2)$$

Where the LL is the liquid limit and $W_{ext.}$ is the extrusion moisture content.

After mixed, the samples were taken to the laminator followed by the extrusion. The ceramic bodies were, then, molded in prismatic shape of 11.0 cm x 2.7cm x 1.7cm. The process of drying and firing has involved temperatures of 110ºC, 750ºC, 800ºC and 850ºC, in an electronic oven. After firing, the ceramic bodies were submitted the tests according to [7] and also to a three loading point flexural strength test according to standard procedure [8]. The obtained results represent the average of 25 determinations. The three loading point flexural strength test was carried out with loading rate of 0.1mm/min with the distance of 9.0 cm between supports.

Results and Discussion

Characterization tests

The following are shown in Fig. 1 the curves of tests performed by wet sieving and sedimentation according to [5] for particle size analysis of clay and coke.

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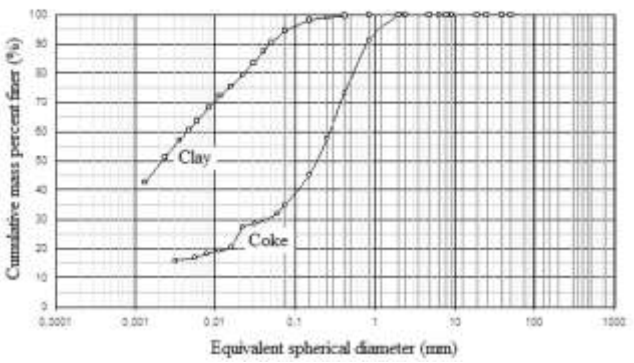


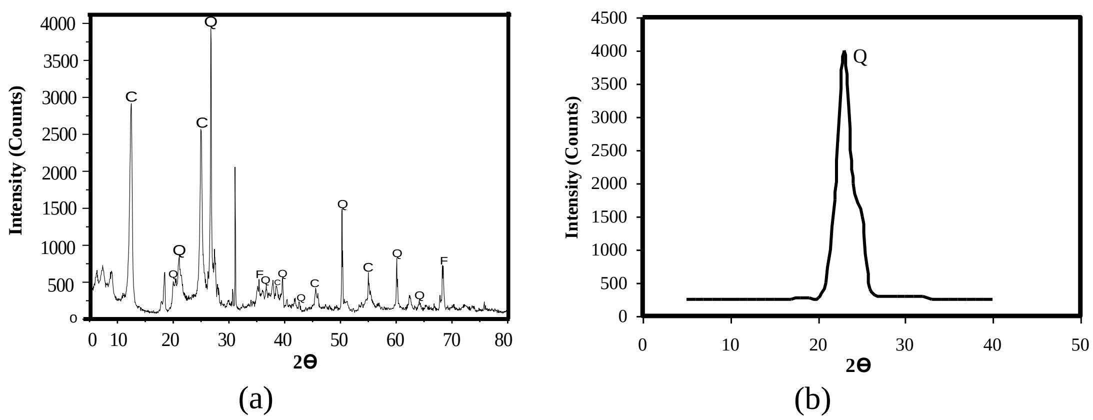
Fig.1. Particle size distribution of the raw materials.

The percentage of clay with particle size below 2 µm, is 49.7%. The coarser fraction of the clay, i.e., with particle size above 20 µm, is 11.2%. In the other hand, the coke has a coarser particle size when compared to that of the clay. As a non-plastic material, however, the coke has a relatively coarse particle size with 68.1% of the particles size above 20 µm.

Tab. 1. Chemical analysis of the raw materials:

raw materials	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	K_2O (%)	TiO_2 (%)	SO_3 (%)	CaO (%)	MnO (%)	V_2O_5 (%)	NiO (%)	C (%)	ZrO_2 (%)	LoI (%)
Clay	45.20	38.76	9.9	2.41	1.69	1.49	0.41	0.10	0.01	----	----	0.03	11.56
Coke	0.74	----	9.8	----	0.84	2.8	0.82	----	0.50	1.21	83.29	----	----

Table 1 shows the chemical composition and the LoI of the raw materials. The chemical composition of the clay is typical of a kaolinite-based material with low amounts of alkaline oxides and relatively high amount of Al_2O_3 (38.76%). The high percentage of LoI (11.56%) indicates an elevated fraction of clay minerals. The chemical composition of the coke, in addition to C (83.29%), confirms the calorific power potential of the coke. The amount of Fe_2O_3 in both raw materials is responsible for the reddish color of the specimen after firing.



(a) (b)

Fig. 2. X-ray pattern of the clay (a) and coke (b). C: kaolinite; Q: quartz; F: feldspar.

The Fig. 2a show the XRD patterns of the clay. These diffractogram indicate that the clay is predominantly kaolinitic with the presence of quartz and feldspar. Also can be observed in Fig. 2b, the amorphous character of the coke showing a peak corresponding to quartz (SiO_2) present as an impurity.

Technological properties

After firing, the samples were carried out physical and mechanical tests mixtures of 0% up to 1.5% of petroleum coke and the results are shown in the following in Figure 2.

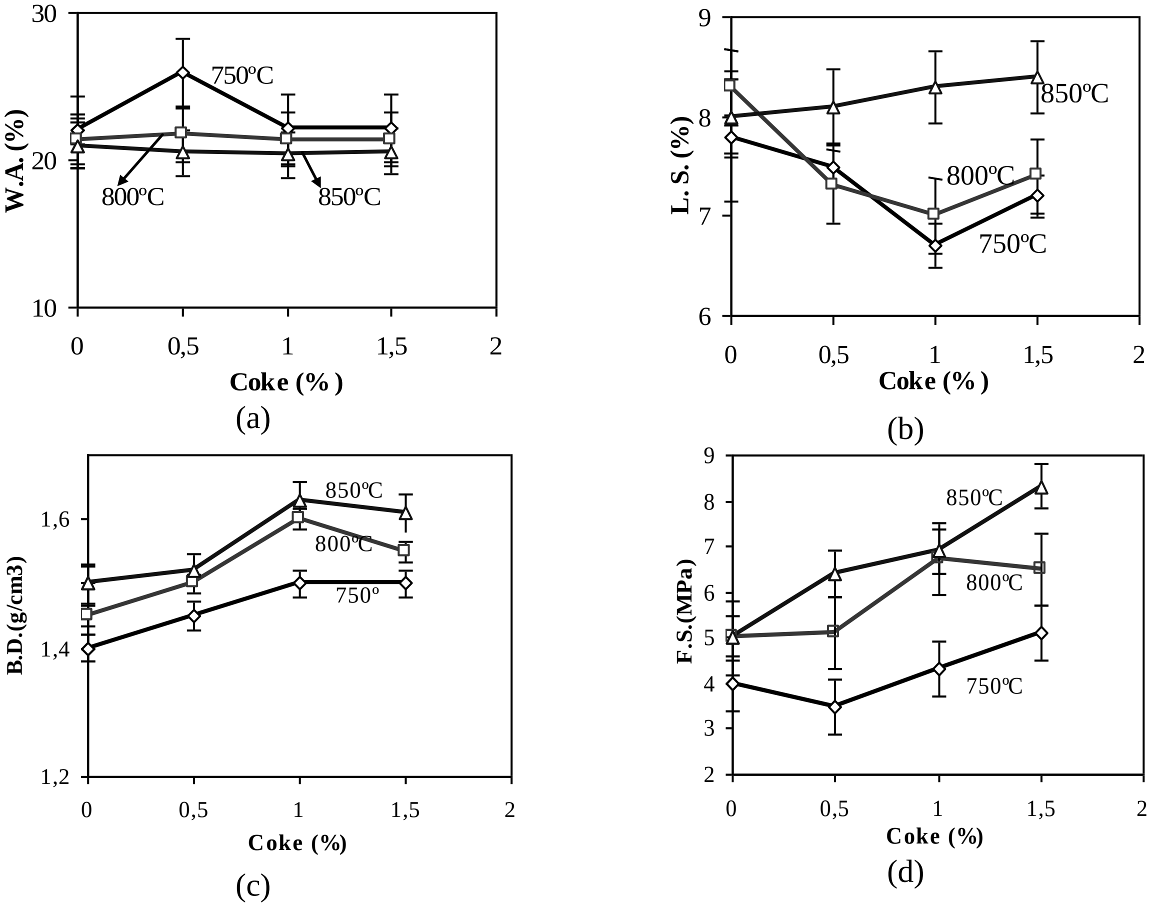


Fig. 2. Technological properties of the mixtures after firing: (a) water absorption; (b) linear shrinkage (c) bulk density; (d) flexural strength.

These results indicate that the petroleum coke addition increases the linear shrinkage to firing 850°C, Fig. 2(b), and the bulk density, Fig. 2(c), while the water absorption, Fig. 7(c) is decreased. Within the error, the flexural strength, Fig. 2(d) remains constant with coke addition to temperature of 800ºC and 850ºC. The results of Fig. 2 (a) shows that the lowest value reached 20.4% water absorption for clay compositions with 1% petroleum coke at 850°C, and the best composition for this property. For linear shrinkage (Fig. 2 (b)), the lowest value was 1% of coke in the ceramic mass and temperature of 750°C, this being indicated composition. For the flexural strength (Fig. 4), the values reached 8.32 MPa at 1.5% coke added in ceramics at 850°C. At 850°C the fluxes cause a small increase in the liquid phase promoting densification [9], therefore, the increased strength, due to the presence of alkali and alkaline earth oxides (Tab.1) in both materials.

Figure 3 shows the Weibull distribution for samples with 0% petroleum coke fired at different temperatures. From this diagram is determined by the Weibull modulus m, which is also considered as the value from which there is a danger of failure, as well as data characterizing the dispersion of the flexural strength [3, 4].

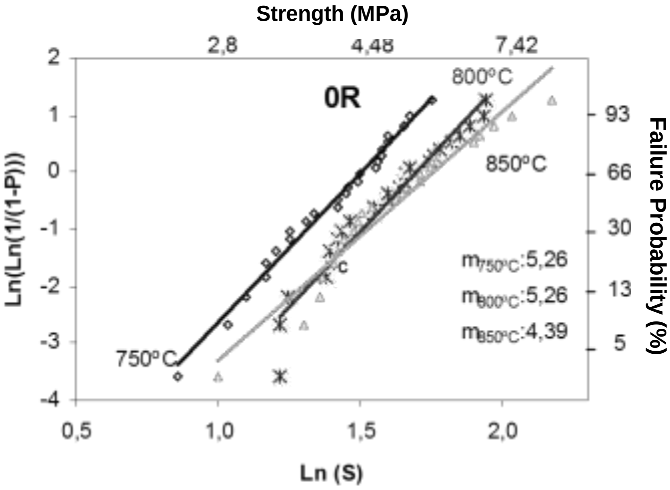


Fig. 3 - Weibull distribution to 0% petroleum coke.

The Fig. 3 shows that the optimum temperature is 800°C, because although their modulus be the same as 750°C their strength fired are higher.

Fig. 4 shows the Weibull distribution for the red ceramic fired at 800°C with different additions of petroleum coke.

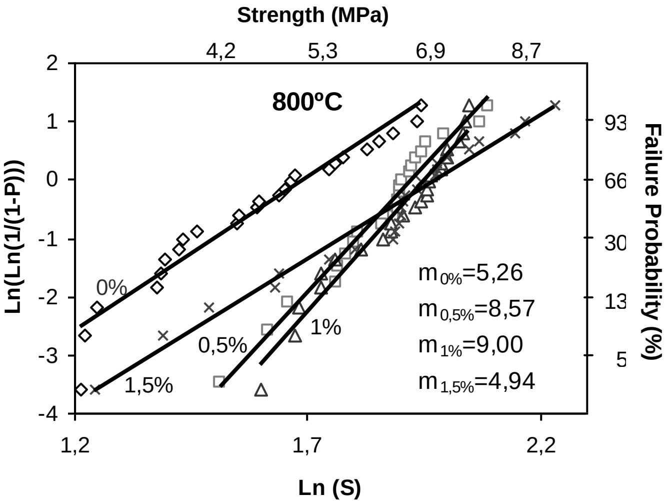


Fig. 4 - Weibull distribution to temperature of 800ºC with different additions of petroleum coke.

In this diagram of the Fig.4, observing Weibull modulus (m), that addition of 1% of petroleum coke in the ceramic body contributed to the set of samples present the greatest value. This incorporation has a high Weibull modulus value of red ceramic materials (m = 9). This indicates that this sample is more homogeneous than in other additions, i.e., lower probability of failure in the presence of manufacture defects and is therefore more reliable.

Conclusion

From the presented results, we can conclude that:

The distribution curve of the particle size of the clay has characteristics of ceramic material for use in red and petroleum coke has a particle size distribution corresponding to sand fraction (68%).

Chemical analysis showed the character refractory clay (SiO2 + Al2O3> 83%) in the presence of fluxing oxides (K_2O+CaO) and that the coke has 83.29% carbon. The presence of the SO_3 was also detected and should be verified how this amount can be damaging at firing, for the equipment of the ceramic industry and to the environment.

With the addition of 1% of petroleum coke is obtained in the ceramic decreases water absorption and greater stability of variation in linear shrinkage, it at 750°C. However, for the samples fired at

800°C with 1% incorporation of coke on the ceramic piece red obtains a significantly improved flexural strength. This conclusion is confirmed when applied to the Weibull distribution.

As seen at 800°C, obtained larger value of Weibull modulus (m = 9) with 1% petroleum coke embedded in ceramic red. Samples without addition of coke showed a lower Weibull modulus (m), meaning that addition up to 1% of the material improved reliability.

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